

# Conductance switching in a molecular device: the role of sidegroups and intermolecular interactions

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We report first-principles studies of electronic transport in monolayers of Tour wires functionalized with different side groups. An analysis of the scattering states and transmission eigenchannels suggests that the functionalization does not strongly affect the resonances responsible for current flow through the monolayer. However, functionalization has a significant effect on the interactions within the monolayer, so that monolayers with NO<sub>2</sub> side groups exhibit local minima associated with twisted conformations of the molecules. We use our results to interpret observations of negative differential resistance and molecular memory in monolayers of NO<sub>2</sub> functionalized molecules in terms of a twisting of the central ring induced by an applied bias potential.

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An important goal in the study of molecular electronics is to identify molecules that can be combined to perform logical functions[1]. In particular, Reed and co-workers [2, 3, 4, 5] have studied the electrical properties of a set of phenyl-ethylene oligomers (known as *Tour wires* (TW)[6]) functionalized with different side groups, and demonstrated that such molecules can show negative differential resistance (NDR)[2, 3] and a "molecular memory"[4, 5] effect, in which case molecules can be switched from a low conductance state to a high conductance state by application of a voltage pulse. A fundamental understanding of the microscopic mechanisms governing the NDR and memory effects in these systems is still lacking.

Complementary studies, by Weiss and co-workers [7], of isolated or small bundles of TWs embedded in a monolayer of spacer alkyl molecules, demonstrated spontaneous conductance switching. While Reed and co-workers only observed switching effects for TWs with NO<sub>2</sub> sidegroups, Weiss et. al. reported spontaneous switching of all the molecules in their study but had limited success in *inducing* switching by using a voltage pulse[7]. Theoretical studies of properties of isolated TWs have emphasized the role of charging of the molecule and subsequent localization/delocalization of molecular orbitals [8, 9] or bias-induced alignment of molecular orbitals on the first and last phenyl rings of twisted TWs[10].

In this paper we use the TranSiesta package[11] to investigate the effect of different sidegroups on both the electrical and structural properties of TW's in self assembled monolayers, and in this way gain new insight into the microscopic origin of the observed NDR and memory effects. TranSiesta is a non-equilibrium Greens function based electronic transport program founded on density functional theory. It treats the entire system selfconsistently under finite bias conditions, and the only major approximation in the method is the choice of exchange correlation(XC) functional. [12] We have previously shown

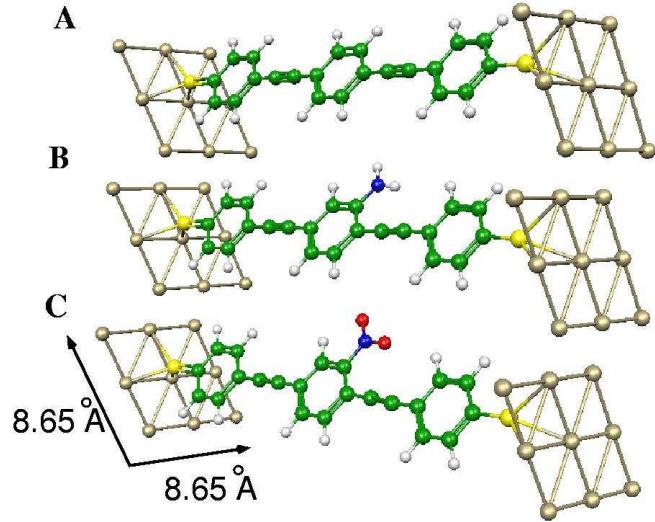


FIG. 1: Geometry of monolayers A, B, and C connected with two Au (111) surfaces. Color codes: C(green), H(white), O(red), N(blue), S(yellow), Au(gold).

that electrical properties of different metallic wires calculated using the method are in excellent agreement with experimental data[13].

The nanopore structures in which NDR and memory effects have been observed are formed by evaporating the molecules onto a small Au surface inside a Si<sub>3</sub>N<sub>4</sub> structure, and then evaporating another Au electrode onto the molecular monolayer[2]. Since there is no detailed information about the structure of the monolayer, our theoretical analysis of the problem proceeds by forming an idealized model of the electrode/monolayer/electrode system and comparing electron transport in three different molecules[14]. We use an Au(111) surface in a 3x3 unit cell for the electrodes and assume the TWs are chemisorbed to the surfaces through strong thiol bonds[15], as illustrated in Fig. 1. monolayer A consists

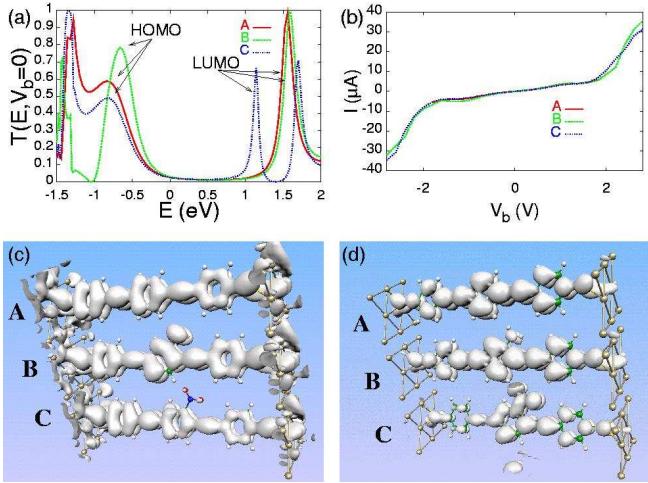


FIG. 2: (a) Zero-bias transmission  $T(E, V_b = 0V)$  versus incident  $E$  for monolayers A, B, and C. HOMO and LUMO resonances are indicated. (b)  $I$ - $V_b$  characteristics for monolayers A, B, and C (c) Isosurface of transmission eigenchannel at the HOMO resonance for monolayers A, B, and C ( $E = -0.84$ ,  $-0.65$ , and  $-0.85$  eV respectively) (d) Isosurface of transmission eigenchannel at the LUMO resonance for monolayers A, B, and C ( $E = 1.56$ ,  $1.59$ , and  $1.14$  eV respectively)

of a bare TW with thiol end groups, while monolayers B and C have been functionalized with  $\text{NH}_2$  and  $\text{NO}_2$  side groups, respectively.

We first investigate the effect of the sidegroups on the electrical properties of the monolayers. The current through the monolayers is determined by the quantum mechanical probability for electrons to tunnel from one electrode to the other, and is calculated using the Landauer formula[16]:  $I = \int_{\mu_L}^{\mu_R} T(E, V_b) dE$ , where  $\mu_{L/R} = \pm eV_b$  and  $T(E, V_b)$  is the transmission probability for electrons incident at an energy  $E$  through a device under a potential bias  $V_b$  (*n.b*  $V_b > 0$  corresponds to hole injection from the right electrode). The general shape of the zero-bias transmission spectra, shown as  $T(E, V_b = 0V)$  in Fig. 2a, is similar for all three systems. The zero bias conductance  $G = \frac{e^2}{h} T(E = \mu_{l/r}, V_b = 0)$ , given by  $2.0 \mu\text{S}$ ,  $2.3 \mu\text{S}$ ,  $1.9 \mu\text{S}$ , for monolayers A, B, and C, is dominated by the tail of a broad highest-occupied-molecular-orbital (HOMO) resonance (at  $E_{\text{HOMO}} = -0.84$ ,  $-0.65$ , and  $-0.85$  eV for monolayers A, B, and C). The narrower lowest-unoccupied-molecular-orbital (LUMO) resonance (at  $E_{\text{LUMO}} = 1.56$ ,  $1.59$ , and  $1.14$  eV for A, B, and C respectively) contributes less to the conductance and thus holes are the dominant carriers. The  $\text{NH}_2$  group is electron donating, so that  $E_{\text{HOMO},B} - E_{\text{HOMO},A} \approx 200$  meV while the  $\text{NO}_2$  group is electron accepting so  $E_{\text{LUMO},C} - E_{\text{LUMO},A} \approx -400$  meV.

To calculate the  $I$ - $V_b$  spectrum we performed self-consistent calculations for biases in the range -2.8 V to 2.8 V in steps of 0.2 V. We note that the charge on the

molecule is *not* fixed[11] and adjusts itself to minimize the free energy[17] as the left/right electrochemical potentials are changed. For all three systems we find that the molecules are close to charge neutrality, and the charge on the molecule  $Q_M$ , as determined by a Mulliken population analysis, change by less than 0.05 e as the bias voltage  $V_b$  is varied. The  $I$ - $V_b$  spectra, shown in Fig. 2b, are very similar, increasing slowly at first but then increasing rapidly around 2V where the resonances come into alignment with the bias window. The main effect of  $V_b$  on  $T(E, V_b)$  is to sample more and more of the resonance while resonant peak height and position vary slowly with  $V_b$ [18].

When the molecules interact with the Au(111) electrodes, the molecular levels broaden into a continuum[16]. The eigenstates of the whole metal/monolayer/metal system consist of scattering states[19, 20], which are molecular orbital-like in the molecule, and Bloch wave-like in the metal slabs. If an orbital is delocalized across the molecule, an electron that enters the molecule at the energy of the orbital has a high probability of reaching the other end and thus there is a corresponding peak in the transmission probability  $T(E, V_b)$ , as illustrated in Fig. 2a. By calculating the continuum eigenstates at the resonance energies ( $E_{\text{HOMO}}, E_{\text{LUMO}}$ ), the orbitals that are responsible for current flow through the molecule can be analyzed. The HOMO resonances, illustrated in Fig. 2c, resemble the HOMO of the isolated molecules while the narrower LUMO resonances, illustrated in Fig. 2d, resemble the LUMO of the isolated molecules. There are minor differences between the orbitals: the  $\text{NH}_2$  side group participates in the HOMO resonance but not in the LUMO resonance, while the  $\text{NO}_2$  group participates in the LUMO resonance and not the HOMO resonance, consistent with their respective donating/accepting characters. It is, however, clear from both the shape of the transmission curves in Fig. 2a and the orbitals in Figs. 2c and 2d that the resonant transmission peaks in monolayers A, B, and C are related to the delocalized nature of the  $\pi$ -orbitals of the bare TWs and is not strongly affected by the functionalization.

The energetics of the monolayers are, however, strongly affected by the functionalization. The triple bond between the phenyl rings is rotationally symmetric and thus constitutes an easy axis about which the middle ring can rotate. The differences in total energy as a function of the rotation angle of the middle ring,  $\theta$ , for the molecules arranged in the 3x3 unit cell of Au(111) are shown in Fig. 3a. The intermolecular interaction energy is strongly dependent on the functionalization: there is a cost of 60 meV (180 meV) to rotate the ring 90° in monolayer A (B), and the flat molecule is clearly favoured. Monolayer C shows a quite different behaviour, it acquires a local minimum at  $\theta = 60^\circ$  and  $120^\circ$ . To understand the origin of these minima we have plotted the

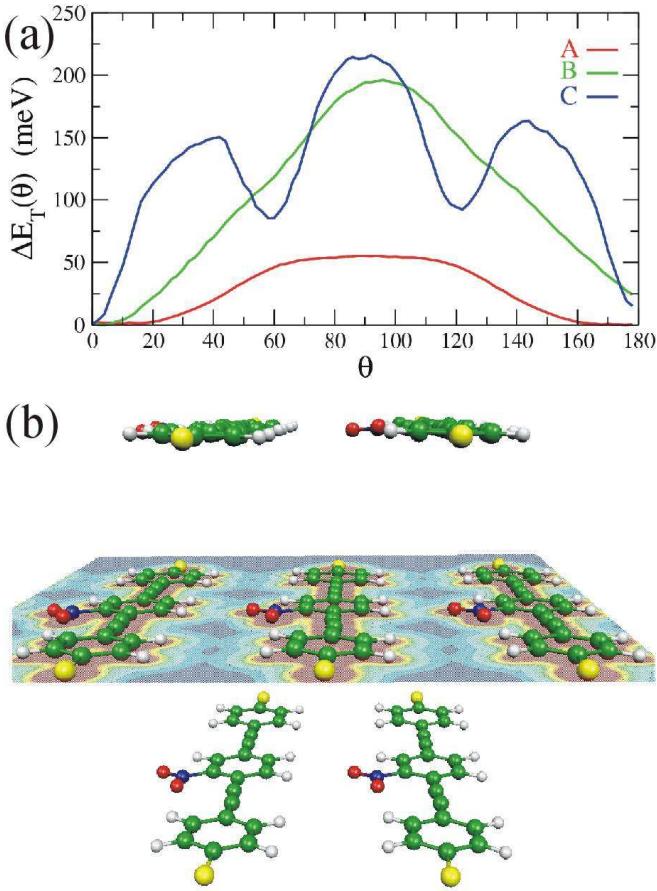


FIG. 3: (a) Energy versus rotation angle for Molecules A, B, and C in Au(111) 3x3 unit cell. The energy is calculated within the Perdew, Burke and Ernzerhof (PBE) approximation for the exchange-correlation functional[21]. (b) Contour plot of the effective potential between TW's with  $\text{NO}_2$  side-groups. Note the bond formation between the O atom and the H atom on the neighboring TW.

effective potential within the monolayer in Fig. 3b. The effective potential reveals the formation of a hydrogen bond between the  $\text{NO}_2$  group and a hydrogen atom on the neighboring TW. Similar hydrogen bond formation involving  $\text{NO}_2$  groups has also been observed in other molecular layers[22]. From Fig. 3b it is also clear that the minima at  $60^\circ$  and  $120^\circ$  can be attributed to bond formation with a new neighboring molecule, and these particular angles arise from the symmetry of the monolayer.

There is a barrier for rotation of the middle ring from  $\theta = 0$  to  $\theta = 60^\circ$  of  $\sim 150$  meV, while the barrier from  $60^\circ$  to  $0^\circ$  is  $\sim 65$  meV. We postulate that, as a voltage pulse is applied, these barriers may change, and a transition to a new molecular conformation with the middle ring twisted may be induced. The local minima only exist when the molecules are functionalized with an  $\text{NO}_2$  side group and thus such transitions only exist when the

molecules are functionalized with an  $\text{NO}_2$  side group [4].

Again because of the lack of detailed information about the monolayer, we have selected a candidate conformation, which we designate monolayer C@60, formed by twisting the middle ring of molecules in monolayer C  $60^\circ$ , for possible stabilization under applied bias. The transmission spectra for monolayer C@60 is shown in Fig. 4a and its  $I-V_b$  characteristics in Fig. 4d. The conductance  $G \approx .12\mu\text{S}$  is roughly 16 times smaller than monolayer C while the current at  $V_b = 2V$  is  $\approx 5$  times smaller. To lowest order,  $G$  is proportional to the product of the matrix elements between  $\pi$ -orbitals on neighbouring phenyl rings so that a rotation of the middle ring will reduce  $G$  by a factor  $\sim \cos^4(\theta) = \frac{1}{8}$ , in rough agreement with the calculated values.

The transmission eigenstates for electrons travelling from left to right at  $E_{\text{HOMO}} = -0.85$  eV and  $E_{\text{LUMO}} = 0.99$  eV are illustrated in Fig. 4b. The HOMO resonance is localized on the phenyl ring nearest the left electrode while the LUMO state corresponds to an orbital of the middle ring, weakly coupled to the first and last rings.

To investigate whether monolayer C@60 could be stabilized with respect to monolayer C as the bias voltage is increased, we show in Fig. 4b the Kohn-Sham total energy of monolayers C and C@60. At  $V_b = 0$ , monolayer C is lower in energy than monolayer C@60. However, when the bias is increased above 2 V, monolayer C@60 becomes lower in energy, leading to an expected conformational change. While there are issues surrounding the evaluation of total energies for such systems [17, 23], Fig. 4b serves to illustrate that different conformations may be stabilized with respect to each other by an external bias. In this case, the calculation suggests a transformation of monolayer C to monolayer C@60 at around 2V. The exact value of the switching voltage will depend on the coverage, detailed structure and size of the monolayer, as well as how the potential drops across the molecules, which can be affected by electrode coupling[18].

The local minima in Fig. 3a are stabilized by the  $\text{NO}_2$  sidegroup, which correlates well with that the molecular memory effect is only observed in monolayers with  $\text{NO}_2$  side groups[4]. Furthermore, the energy barrier for rotation of  $65 - 150$  meV derived from our crude model is in rough agreement with the 80 meV barrier height extracted from bit retention times[4], thus conformational changes stabilized by intermolecular interactions is a good candidate for explaining such phenomena.

Because the minima emerge from interactions within the monolayers, the above effects may only be observed in nanopore experiments [2, 3, 4, 5] and not in experiments of single molecules. In the STM experiments of Weiss and co-workers[7] on single or small bundles of molecules, the conductance switching may be related to different conformations formed by steric interactions between the TWs and the insulating alkyl molecules. This could explain

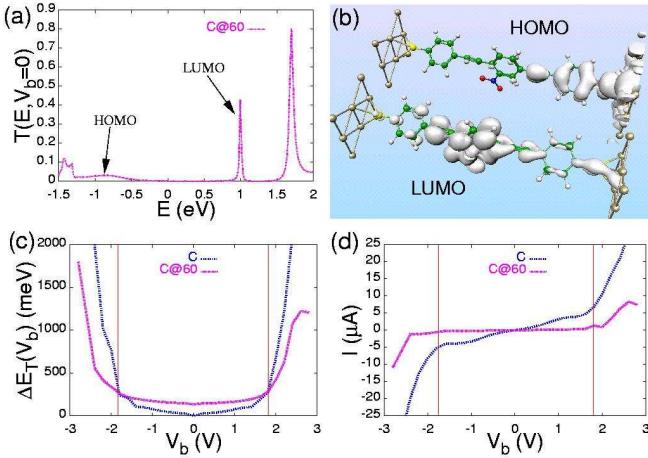


FIG. 4: (a) Zero-bias transmission  $T(E, V_b = 0)$  for monolayer C@60. (b) Transmission eigenchannels corresponding to HOMO and LUMO resonances of C@60. (c) Total energy of monolayer C(blue) and monolayer C@60(magenta) as a function of bias potential. (d)  $I$ - $V_b$  characteristics of monolayer C(blue) and monolayer C@60(magenta).

why the observed switching behaviour was independent of the functionalization of the molecules.

In conclusion, we find that functionalization of TWs has a stronger effect on the energetics of the monolayers than on the orbitals responsible for current transport and a better understanding of the intermolecular interactions in such monolayers could hopefully be exploited in order to design molecular electronic devices with specific properties.

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